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Kinetic evidence for the structural similarity between a supercooled liquid and an icosahedral phase in $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ bulk metallic glass

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By differential scanning calorimetric measurement, the kinetics of the phase transformation present in $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ bulk metallic glass during continuous heating was investigated. It was found that the effective activation energy from a supercooled liquid to an icosahedral quasicrystalline phase is much lower than that from the supercooled liquid to eutectic crystalline phases. In addition, the activation energy from the icosahedral phase to the crystalline phases is almost the same as that from the supercooled liquid to the crystalline phases. Both of them support that the local atomic structure is similar for the supercooled liquid and the icosahedral phase in the bulk metallic glass. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1383060]

The structure of metallic glasses and supercooled liquids is a long-standing issue in solid-state physics and materials science.[1–6] Following the discovery of a Au–Si metallic glass by rapid cooling of a metallic melt,[7] various models have been proposed to describe the structure of metallic glasses.[2] Since icosahedral clusters lack long-range periodic translational order,[8] theoretical and computer-simulated results suggested that icosahedral clusters are the preferred structural units in supercooled liquids and metallic glasses.[9–12] However, except for limited pair-distribution-function and electron energy-loss spectroscopy results,[13–15] supplementary evidence from other techniques supporting the structural model is still missing. Calorimetry has traditionally been valuable for identification of the structural evolution of metallic glasses. However, kinetic evidence on the structural model has not been obtained due to the thermal instability of metallic glasses that form icosahedral quasicrystalline phases, such as some Al-based metallic glasses. Recently, a bulk metallic glass with excellent thermal stability was discovered, in which three different exothermic reactions: *a supercooled liquid to an icosahedral quasicrystalline phase, the residual supercooled liquid to crystalline phases, and the icosahedral phase to the crystalline phases*, subsequently occur during continuously heating.[16,17] This makes it possible to explore the kinetic relationship between the supercooled liquid and the icosahedral phase. Here, we report kinetic evidence for the structural similarity between the supercooled liquid and the icosahedral structure in Zr-based bulk metallic glass.

Our experiments were performed on a $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ metallic glass prepared by melt spinning. The amorphous nature of the as-quenched samples has been confirmed by transmission electron microscopic (TEM) observations and electron diffraction. The differential scanning calorimeter (DSC) measurement was carried out under an argon atmosphere at heating rates ranging from 5 to 80 K/min. The products of each exothermic reaction appearing in the DSC traces were identified by x-ray diffraction (XRD) and TEM analyses. Samples used for phase identification were prepared under DSC at a heating rate of 5 K/min. When the samples sealed in Al pans were heated up to the designed temperatures, which are around each reaction peak, they were quickly moved out of the DSC unit and then quenched into water. TEM observations were performed under a Topcon-2B analytical electron microscope with an operating voltage of 200 kV. XRD analysis was carried out by conventional x-ray diffractometry ($\mathrm{Cu}\,K\alpha$).

Figure 1 shows the DSC traces measured at heating rates ranging from 5 to 80 K/min. The glass transition points and the exothermic peaks all shift to higher temperatures with the increase of the heating rates. In addition, at lower heating rates (5–20 K/min), three exothermic peaks can be observed, and with the increase of heating rates, the second exothermic peak gradually merges into the third peak. To identify the

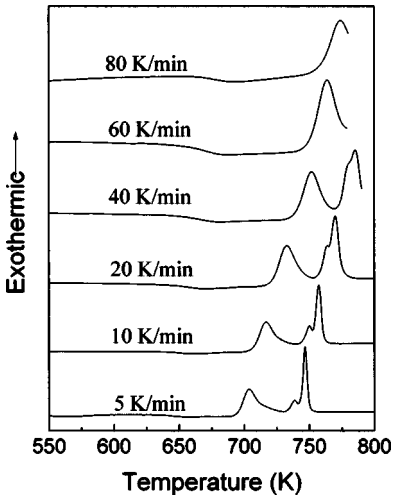

FIG. 1. Differential scanning calorimeter (DSC) scanning traces at constant heating rates of 5, 10, 20, 40, 60, and 80 K/min, respectively.

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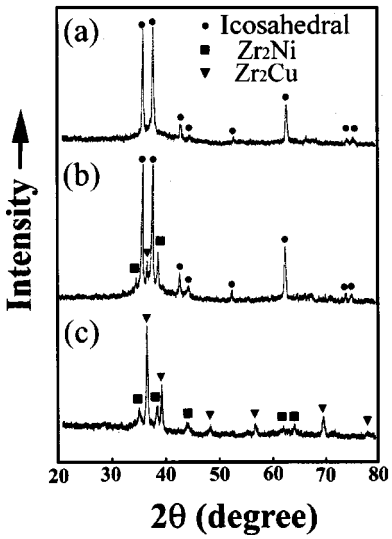

FIG. 2. X-ray diffraction patterns corresponding to different annealing stages of the alloy under DSC at a heating rate of 5 K/min. (a) Samples heated up to 730 K, just higher than that of the first exothermic peak; (b) samples heated up to 740 K, within the second exothermic peak; and (c) the sample heated up to 760 K.

phases present in the bulk metallic glass during continuously heating, TEM and XRD analyses were employed. Figure 3 shows the XRD spectra of the samples heated up to different temperatures at a heating rate of 5 K/min. In the spectrum of the samples heated up to 730 K [Fig. 2(a)], which is just higher than the peak temperature of the first exothermic reaction, only an icosahedral phase can be identified. When the samples were heated up to 740 K, which is within the second exothermic peak, the XRD spectrum [Fig. 2(b)] shows that two crystalline phases, Zr_2Cu and Zr_2Ni, appear, and the diffraction peaks of the icosahedral phase still maintain high intensity. After the samples were heated up to 760 K, which is higher than the peak temperature of the third exothermic reaction, only crystalline phases, Zr_2Cu and Zr_2Ni, can be identified in the spectrum [Fig. 2(c)]. This suggests that the icosahedral phase transforms into the crystalline phases by the third exothermic reaction. Separate TEM observation shows that in the samples heated up to 730 K, only an icosahedral phase with a size of hundreds of nanometers precipitates from the supercooled liquid, and a small amount of the residual amorphous remains among the icosahedral grains [Fig. 3(a)]. When the samples were heated up to 740 K, the intergranular residual amorphous first decomposes into crystalline phases with a lamellar structure. In addition, it can be observed that lamellar crystals always grow into icosahedral grains [Fig. 3(b)]. The appearance of the lamellar structure indicates that the formation of the two crystalline phases, Zr_2Cu and Zr_2Ni, may be by a eutectic reaction. Previous work demonstrated that no compositional difference between the icosahedral phase and the residual amorphous is detected, and the transformation from the supercooled liquid to the icosahedral phase can be considered as polymorphic type.[16,17] In addition, at this annealing stage, the lamellar crystals can be occasionally observed within some icosahedral grains. Combined with the XRD result, it can be deduced that the transformation from the icosahedral phase to the crystalline Zr_2Cu and Zr_2Ni phases may also be by a eutectic-like reaction. Thus, the composition of the alloy may

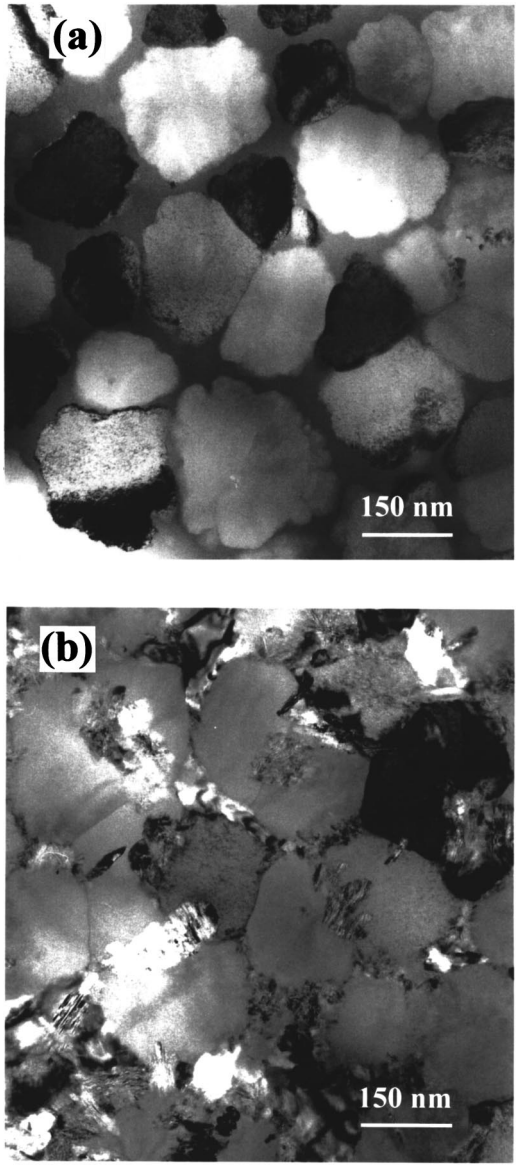

FIG. 3. Bright-field TEM images of samples heated up to (a) 730 K and (b) 740 K.

be close to a eutectic point in the Zr–Cu–Ni–Al–Ag quinary system. Based on the TEM and XRD observations, it is clarified that the three exothermic reactions appearing in the DSC traces with lower heating rates correspond to three different kinds of the phase transformations: *the supercooled liquid to the icosahedral quasicrystalline phase, the residual supercooled liquid to the crystalline* Zr_2Cu *and* Zr_2Ni *phases, and the icosahedral phase to the same crystalline phases,* Zr_2Cu *and* Zr_2Ni.

The variation of DSC traces with heating rates, as shown in Fig. 1, demonstrates that the heating rates clearly influence the phase transformation temperatures. The effective activation energies **E** for the glass transition and the exothermic reactions are calculated by Kissinger's equation:[18]

$$\mathrm{Ln}\, Y \equiv \ln \frac{T_c^2}{R} = \ln \frac{E}{K_0 \kappa_B} + \frac{E}{\kappa_B T_c},$$

where $\mathbf{T_c}$ are the critical points corresponding to the glass transition $\mathbf{T_g}$, and the exothermic peaks $\mathbf{T_{p1}}$, $\mathbf{T_{p2}}$, and $\mathbf{T_{p3}}$ in Fig. 1; **R** is the heating rate; κ_B is the Boltzman constant;

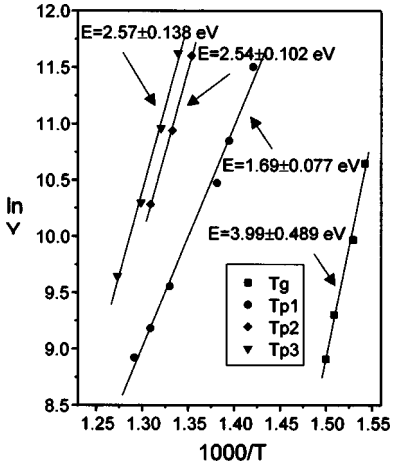

FIG. 4. Effective activation energies of the each reaction present in the alloy during continuous heating. The linear relationships were plotted according to Kissinger's equation. $\mathbf{T_g}$, $\mathbf{T_{p1}}$, $\mathbf{T_{p2}}$, and $\mathbf{T_{p3}}$ are the glass transition temperature, and the peak temperatures of the first, second, and third exothermic reactions in Fig. 1, respectively.

and $\mathbf{K_0}$ is a constant. Figure 4 exhibits the linear relationships between $\ln(\mathbf{T}_c^2/\mathbf{R})$ and $\mathbf{1}/\mathbf{T_c}$ for the glass transition and the three exothermic phase transformations. The slopes of each line correspond to the effective activation energies of the each reaction. The activation energy of the glass transition is much higher than that of the exothermic reactions. Moreover, the activation energy from the supercooled liquid to the icosahedral phase is much lower than that of the residual supercooled liquid to the eutectic crystalline phases. In addition, the activation energy from the icosahedral phase to the crystalline phases is almost the same as that from the residual supercooled liquid to the crystalline phases. Generally, the activation energy is regarded as the extra energy needed to surmount short-range barriers coming from neighbor atoms during local atomic structure evolution. Almost the same values suggest that the local structural units involving the neighbor atoms may be quite similar for the supercooled liquid and the icosahedral phase. The additional evidence to support the structural similarity is that the lower activation energy from the supercooled liquid to the icosahedral phase indicates that less atomic reconstruction is required during the formation of the icosahedral phase from the supercooled liquid.

In summary, the devitrification kinetics from the supercooled liquid to the icosahedral phase, the supercooled liquid to the eutectic crystalline phases, and the icosahedral phase to the crystalline phases, were investigated during continuous heating in $Zr_{65}Al_{7.5}Ni_{10}Cu_{12.5}Ag_5$ bulk metallic glass. The measured kinetic parameters exhibit an interesting relationship between the supercooled liquid and the icosahedral phase, which strongly supports that the local atomic structure is similar for the two phases.

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